



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(21) International Application Number:</b> PCT/GB97/02565 <b>(22) International Filing Date:</b> 19 September 1997 (19.09.97) <b>(30) Priority Data:</b> 9620808.7 5 October 1996 (05.10.96) GB 9701911.1 30 January 1997 (30.01.97) GB <b>(71) Applicant (for all designated States except US):</b> TIOXIDE SPECIALTIES LIMITED [GB/GB]; Lincoln House, 137-143 Hammersmith Road, London W14 0QL (GB). <b>(72) Inventors; and</b> <b>(75) Inventors/Applicants (for US only):</b> SKINNER, Christopher, John [GB/GB]; 67 Alnwick Road, Newton Hall, Durham DH1 5NN (GB). RIDLAND, John [GB/GB]; 12 Oatlands Way, The Mount, Durham DH1 5GL (GB). <b>(74) Agents:</b> JACKSON, John, Derek et al.; ICI Group Intellectual Property, P.O. Box 90, Wilton, Middlesbrough, Cleveland TS90 8JE (GB).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (GH, KE, LS, MW, SD, SZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> CATALYSTS  <b>(57) Abstract</b>  A catalyst, suitable for use in polyurethane compositions comprises the reaction product of: (a) the reaction product of a titanium, zirconium, hafnium or aluminium orthoester and a $\beta$ -diketone or $\beta$ -ketoester and (b) a complexing agent selected from a mercapto compound, an oxazolidine or a tetrahydro-oxazine. The catalyst is particularly useful for preparing coating compositions which have a long pot life and can be cured at room temperature.		

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## CATALYSTS

This invention relates to catalysts and in particular to catalysts for use in the preparation of polyurethanes.

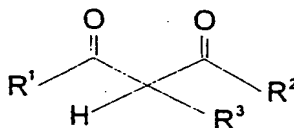
There is currently much change in the industrial coatings market place.

5 Coating applications are becoming increasingly more demanding in terms of performance, safety and environmental compliance. Many traditional coating chemistries are finding it impossible to survive in this rapidly changing climate. Polyurethane coatings has been one technology that has enjoyed substantial growth in this field and their success lies in the fact that polyurethane coatings provide superior chemical resistance, flexibility,  
 10 abrasion resistance, weathering and impact resistance. The protection afforded by such coatings is of particular significance in the automotive, construction, marine and chemical sectors.

Polyurethane coatings, films, sealants and foams are made by reacting hydroxyl containing polymers and polyisocyanates according to the isocyanate addition  
 15 polymerisation process. The reaction between the isocyanate groups and the active hydrogen atoms of the hydroxyl containing polymer is usually accelerated by the means of catalysts. Tertiary amines and metal compounds have been used as catalysts, examples being triethylene diamine, tin(II) octoate and di-*n*-butyl tin dilaurate. However, the prior art catalysts have disadvantages. In the case of amines, this is manifested by lower catalytic  
 20 activity mol per mol than metal based catalysts, odour and toxicity. Many of the traditional metal catalysts also demonstrate an activity that is high but difficult to control appropriately for some applications.

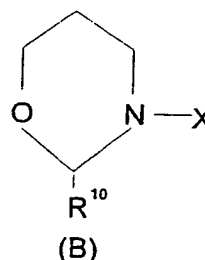
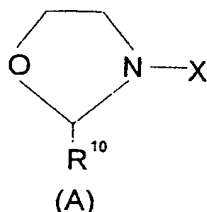
According to the invention, there is provided a catalyst comprising the reaction product of:

- 25 (a) the reaction product of a titanium, zirconium, hafnium or aluminium orthoester and a  $\beta$ -diketone or  $\beta$ -ketoester having the general formula



where R<sup>1</sup>, R<sup>2</sup> and R<sup>3</sup> may be independently selected from the group consisting of hydrogen and alkyl, aryl, cycloalkyl, alkoxy, aryloxy, hydroxyalkyl, alkoxyalkyl and  
 30 hydroxyalkoxyalkyl groups containing up to eight carbon atoms; and

(b) a complexing agent selected from a mercapto compound or an oxazolidine or a tetrahydro-oxazine having the general formula (A) or (B) respectively,



in which  $R^{10}$  is hydrogen or an alkyl group and X is a hydroxyalkyl group, or mixtures thereof.

Preferably, the orthoester has the formula  $M(OR)_4$ , in which M is titanium or zirconium and R is an alkyl group, a cycloalkyl group or an aryl group. More preferably R contains 1 to 8 carbon atoms and particularly suitable orthoesters include tetraisopropoxy titanium, tetra-*n*-butoxy titanium, tetra-*n*-propoxy zirconium and tetra-*n*-butoxy zirconium.

Preferably the  $\beta$ -diketone or  $\beta$ -ketoester is selected from acetylacetone, methylacetoacetate, ethylacetoacetate or *tert*-butylacetoacetate and the molar ratio of titanium, zirconium, hafnium or aluminium orthoester to the  $\beta$ -diketone or  $\beta$ -ketoester is from 1:0.5 to 1:4. Reaction products of mixtures of both types of ligand and of titanium, zirconium, hafnium or aluminium orthoesters containing more than one alkoxy group are within the scope of the invention. More preferably the  $\beta$ -diketone or  $\beta$ -ketoester is acetylacetone or ethylacetoacetate and the molar ratio of titanium, zirconium, hafnium or aluminium orthoester to acetylacetone or ethylacetoacetate is from 1:1 to 1:4.

A variety of mono-functional or poly-functional mercaptans can be used to advantage. Representative mercaptans include, for example, trimethylol propane trithioglycolate, pentaerythritol *tetrakis*-(3-mercapto propionate), ethylene glycol *bis*-(3-mercapto propionate), ethylene glycol di-mercapto acetate, mercapto propionic acid and esters thereof, trimethylol propane *tris*-(3-mercaptopropionate), toluene-3,4-dithiol,  $\alpha$ ,  $\alpha'$ -dimercapto-*p*-xylene, dodecane dithiol, didodecane dithiol, 3,4-dimercaptotoluene, dimercapto benzothiazole, allyl mercaptan, methylthioglycolate, benzyl mercaptan, 1-octane thiol, para-thiocresol, cyclohexyl mercaptan, dithioerythritol, 6-ethoxy-2-mercaptobenzothiazole, 1,6-hexane dithiol, *d*-limonene dimercaptan, and the like and mixtures thereof. In addition to monofunctional or polyfunctional mercaptans, monomer or oligomer compounds can be synthesised or modified to contain pendant mercaptan or thiol groups.

Preferably, the mercapto compound is selected from trimethylolpropane

*tris*-(3-mercaptopropionate), pentaerythritol *tetrakis*-(3-mercaptopropionate), ethylene glycol *bis*-(3-mercaptopropionate) and pentaerythritol *tetrakis*-(2-mercaptoacetate) and mixtures thereof. More preferably the mercapto compound is selected from pentaerythritol *tetrakis*-(3-mercaptopropionate), ethylene glycol *bis*-(3-mercaptopropionate) and  
5 pentaerythritol *tetrakis*-(2-mercaptoacetate) and mixtures thereof.

In one embodiment, the complexing agent is an oxazolidine or a tetrahydro-oxazine having the formula (A) or (B) respectively as hereinbefore defined. Preferred complexing agents of this embodiment are oxazolidines having formula (A).

In formula (A) or (B), R<sup>10</sup> is hydrogen or an alkyl group preferably  
10 containing up to 8 carbon atoms. Suitable alkyl groups include methyl, ethyl, propyl, isopropyl and butyl groups. X is a hydroxyalkyl group preferably containing up to 6 and more preferably up to 4 carbon atoms. Particularly preferred complexing agents are compounds in which X is a hydroxyethyl or a hydroxypropyl group.

Sufficient complexing agent must be present relative to the reaction  
15 product of a titanium, zirconium, hafnium or aluminium orthoester and a  $\beta$ -diketone or  $\beta$ -ketoester in order that the hydroxyl containing polymer/ polyisocyanate reaction mixture containing the catalyst has a pot life suitable for the particular application. The pot life of a reaction mixture is normally defined as the time required for the viscosity of the mixture in an open pot to double from its initial viscosity.

20 The catalyst of the present invention provides the ability to formulate a catalysed reaction mixture which has a very long and useful pot life without the need for formulating specifically designed resins, curing agents, or the like. A further advantage is that the catalysed reaction mixture need not be heated to achieve cure, although it can be heat cured if desired. Furthermore it is often found that utilisation of the catalyst of this  
25 invention will allow lower cure temperatures or shorter cure times when compared to standard catalyst technology. Yet another advantage is the ability to form harder and more corrosion resistant films than allowed by previous catalyst technology.

The catalyst of the invention is usually added to the reaction mixture in an amount in the range 0.005 per cent to 0.5 per cent by weight with respect to weight of  
30 reaction mixture.

Conventional urethane coatings may be provided as two separate packages (a two-pack system). One component (Part 1), typically, is the hydroxyl containing polymer while the second component (Part 2) is the polyisocyanate. Solvents and other conventional paint additives may be added to each component in accordance  
35 with conventional teachings. The catalyst is often included in the hydroxyl containing

polymer to avoid premature gelation of the polyisocyanate. Occasionally, the catalyst package is not added to either Part 1 or Part 2 until just prior to application of the coating composition. Application of conventional two-pack coating compositions typically takes place by the admixture of the two components just before application which may be by  
5 conventional roll coat, reverse rollcoat, or other conventional tactile means; or can be by spray techniques. Regardless of the application technique, the two components are kept separate in order to prevent premature reaction with attendant viscosity increase which prevents effective application. The applied coatings are often baked in order to speed the cure and ensure expulsion of solvent and gases from the applied film.

10 The invention also provides for the use of the catalyst as hereinbefore defined in the reaction between a hydroxyl containing polymer or mixture of hydroxyl containing polymers and an isocyanate containing compound or a mixture of isocyanate containing compounds.

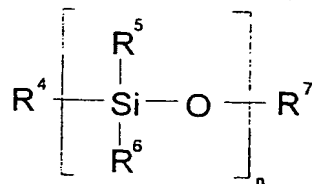
The hydroxyl containing polymers for use in the present invention include  
15 in particular polyesters, polyesteramides, polyethers, siloxanes and/or silicones and copolymers of such materials having hydroxyl functionality within their structure.

Examples of the polyesters are those predominately hydroxyl terminated polyesters prepared from dicarboxylic acids including, but not restricted to, succinic, glutaric, adipic, pimelic, azelaic and sebacic acids. Polybasic acids obtained by the  
20 polymerisation of unsaturated long-chain fatty acids obtained from naturally occurring oils may be used. Mixtures of acids may also be used. Suitable glycols for use in the preparation of polyesters include but are not restricted to ethylene glycol, 1,2-propyleneglycol, 1,3-butylene glycol, diethylene glycol, triethylene glycol and decamethylene glycol. Mixtures of glycols may be used. Branching groups containing  
25 more than two isocyanate reactive groups may also be used. Suitable branching components include polyhydric alcohols such as glycerol, pentaerythritol, sorbitol and polycarboxylic acids such as tricarballylic acid and pyromellitic acid and compounds containing mixed functional groups such as diethanolamine and dihydroxystearic acid.

The polyethers may be any hydroxyl containing polymers or co-polymers  
30 made by the polymerisation or co-polymerisation of cyclic ethers such as epichlorohydrin, tetrahydrofuran, oxacyclobutane and substituted oxacyclobutanes and 1,2-alkylene oxides, for example, ethylene oxide and 1,2-propylene oxide. Alternatively there may be used branched polyethers prepared, for example, by polymerising an alkylene oxide in the presence of a substance having more than two active hydrogen atoms, for example,

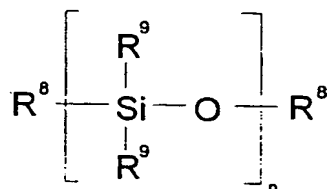
glycerol, pentaerythritol and ethylene diamine. Mixtures of linear and branched polyethers may be used.

Siloxanes may also be referred to as polyoxysilanes, and are sometimes simply referred to as polysilanes. Herein, siloxane refers to compositions having the  
5 formula



where n is from 1 to 10 when no solvents are present in the composition. When solvents are included in the composition, n may be higher than 10. In this formula R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> is independently selected from the group consisting of hydrogen and alkyl, aryl, cycloalkyl,  
10 alkoxy, aryloxy, hydroxyalkyl, alkoxyalkyl and hydroxyalkoxyalkyl groups containing up to six carbons. R<sup>7</sup> is selected from the group consisting of hydrogen and alkyl and aryl groups. In most cases, at least two of the R<sup>4</sup>, R<sup>5</sup> and R<sup>6</sup> groups are hydrolysable oxy substituents which can form polymers by hydrolysis.

Silicone refers to compositions having the formula



15 where each R<sup>9</sup> is independently selected from the group consisting of the hydroxyl group and alkyl, aryl and alkoxy groups having up to six carbons, each R<sup>8</sup> is independently selected from the group consisting of hydrogen and alkyl and aryl groups having up to twelve carbons and n is from 1 to 10 when no solvents are present in the composition.

20 When solvents are included in the composition, n may be higher than 10.

Isocyanate containing compounds crosslink with the hydroxyl groups of the resin or polymer under the influence of the metal catalyst to cure the coating. Aromatic, aliphatic, or mixed aromatic/aliphatic isocyanates may be used. Further, alcohol-modified and alternatively modified isocyanate compositions can be used. Poly-isocyanates  
25 preferably will have from about 2 to 4 isocyanate groups per molecule. Suitable poly-isocyanates include, for example, hexamethylene diisocyanate, polymethyl polyphenyl isocyanate (Polymeric MDI or PAPI), 4,4'-toluene diisocyanate (TDI), diphenylmethane diisocyanate (MDI), *m*- and *p*-phenylene diisocyanates,

*tris*-(4-isocyanatophenyl) thiophosphate, triphenylmethane triisocyanate, dicyclohexylmethane diisocyanate ( $H_{12}$ MDI), cyclohexane diisocyanate (CHDI), bis-isocyanatomethyl cyclohexane ( $H_6$ XDI), trimethylhexane diisocyanate, dimer acid diisocyanate (DDI), trimethyl hexamethylene diisocyanate, dicyclohexylmethane diisocyanate and dimethyl derivatives thereof, lysine diisocyanate and its methyl ester, isophorone diisocyanate, methyl cyclohexane diisocyanate, 1,5-naphthalene diisocyanate, triphenyl methane triisocyanate, xylene diisocyanate and methyl and hydrogenated derivatives thereof, polymethylene polyphenyl isocyanates, chlorophenylene-2,4-diisocyanate, and mixtures thereof. Aromatic and aliphatic polyisocyanate dimers, trimers, oligomers, polymers (including biuret and isocyanurate derivatives) and isocyanate functional prepolymers are often available as preformed packages and such packages are also suitable for use. The ratio of isocyanate equivalents of the polyisocyanate cross-linking agents to the hydroxyl groups of the hydroxy materials preferably should be greater than 1:1 and can range from 1:2 up to 2:1. The precise intended application of the coating composition will often dictate this ratio which is known as the isocyanate index.

A solvent or vehicle may be included as part of the coating composition. Volatile organic solvents may include ketones and esters for minimising viscosity, though some aromatic solvent may be used and typically such solvents are part of the volatiles contained in commercial isocyanate polymers. Representative volatile organic solvents include, for example, methyl ethyl ketone, acetone, butyl acetate, methyl amyl ketone, methyl isobutyl ketone, ethylene glycol monoethyl ether acetate (sold under the Trademark Cellosolve acetate) and the like. Organic solvents commercially utilised in polyisocyanate polymers include, for example, toluene, xylene and the like. The effective non-volatile solids content of the coating composition can be increased by incorporation of a plasticiser ester which is non-volatile or has a relatively low volatility (high boiling point) and which is retained for the most part in the cured film. Such suitable plasticiser esters include, for example, di-(2-ethylhexyl) phthalate (DOP) and the like. If used, the proportion of plasticiser ester should not exceed 10% by weight; otherwise loss of mar resistance can occur. Typically, the proportion of plasticiser ester, when used, is in the range 5 to 10% by weight. The coating composition can additionally contain opacifying pigments and inert extenders such as, for example, titanium dioxide, zinc oxide, clays such as kaolinite clays, silica, talc, carbon or graphite (e.g. for conductive coatings) and the like. Additionally, the coating compositions can contain tinctorial pigments, corrosion-inhibiting pigments, and a variety of agents typically found in coating



compositions. Such additional additives include, for example, surfactants, flow or levelling agents, pigment dispersants and moisture scavengers based on systems such as oxazolidines and the like.

Using the catalyst of the invention, a coating composition can be  
5 formulated to have a minimum pot life of at least 2 hours in an open pot and generally the coating can be formulated to have a pot life which is in the range 2 to 8 hours. Such extended pot life is desirable and means that refilling the pot at the plant during shifts is not usually required. After storage of the coating composition, the stored composition can be modified to application viscosity with suitable solvent (if required) and such a  
10 composition retains all the excellent performance characteristics which it initially possessed.

Heat curing of coatings generally involves baking the applied coating composition at temperatures ranging from 50°C to 150°C or higher for time periods ranging from 1 to 30 minutes. Heating of the coated substrate can be beneficial for  
15 solvent expulsion from the film as well as ensuring that the film is non-blocking for rapid handling of the coated substrate. The heating schedules needed for the catalyst of this invention tend to be rather mild in terms of temperature and time compared to conventional heat-cured urethane systems.

A variety of substrates can be coated with the coating compositions  
20 prepared according to the present invention. Substrates include metal, such as, for example, iron, steel, aluminium, copper, galvanised steel, zinc, and the like. Additionally, the coating composition can be applied to wood, glass, concrete, fibreboard, RIM (reaction injection moulded urethanes), SMC (sheet moulding compound), vinyl, acrylic, polyolefine and other polymeric or plastic material, paper and the like. Since the coating  
25 compositions can be cured at room temperature, thermal damage to thermally-sensitive substrates is not a limitation on use of the coating compositions. Further, with the ability to use the vaporous amine catalyst spray method, the flexibility in use of the coating compositions is enhanced even further. It should be understood, however, that heating of the coating composition following application (e.g. to a temperature between about 50°C  
30 and 150°C) is often recommended for enhancing solvent expulsion.

The coatings which are made available by this invention can be used as primers, intermediate coats, and top coats and the cure is substantially independent of film thickness.

The invention will be more readily understood from the following examples in which all percentages and proportions are by weight, unless otherwise expressly indicated.

**EXAMPLE 1****Preparation of Catalyst A**

0.1 mol of tetra-n-propoxy zirconium (Tilcom® NPZ from Tioxide Specialties Ltd.) was added to a 1 litre flask placed in a cold water bath and 0.1 mol of ethylacetoacetate was added over a period of one hour whilst the mixture was stirred. The resulting product was a pale yellow liquid. The zirconium content of the catalyst was measured at 15.85%.

4 mmol of this product was added to a 50 ml flask placed in a cold water bath and 40 mmol of pentaerythritol *tetrakis*-(mercapto- propionate) was added. The resulting product was a clear mobile liquid. The zirconium content of the catalyst was measured at 1.54%

**Comparative Catalyst**

Dibutyl tin dilaurate (source Aldrich Chemicals) was used as the comparative catalyst.

15 **Testing of the Catalysts in Film Formation (at an addition level to give molar% Zr equal to molar% Sn)**

108 g of an acrylic resin (Joncryl 500 from S.C. Johnson Polymer b.v.), 40.93 g of methyl *n*-amyl ketone and the calculated amount of catalyst were thoroughly mixed. To this container 39.42 g of an isocyanate (Desmodur® LS2025 from Bayer) was added. From the mixture, drawdowns (wet film thickness 60 micrometre) on glass plates were made. Each plate was then cured and the hardness of the resulting film measured. The viscosity of the remaining mixture was then measured using a Brookfield viscometer every 0.5 hr.

**Viscosity of Hydroxyl Containing Polymer / Isocyanate Mixture vs. Time**

Time (hrs)	Comparative Catalyst (0.06g)	Catalyst A (0.73g)
0	260	138.3
0.5	Gelled	153.3
1		176.7
1.5		181.7
2		185
2.5		185
3		191.7
3.5		191.7
4		191.7

**Film Hardness by Pendulum Testing of Resulting Films**

Cure Schedule	Comparative Catalyst	Catalyst A
ambient 120hrs	64 s	79 s

**EXAMPLE 2**

The same catalyst and comparative catalyst as in Example 1 were used.

5 **Testing in Film Formation of the Catalysts (at an addition level to give molar % Zr equal to molar % Sn)**

108 g of an acrylic resin (Joncryl 500 from S.C. Johnson Polymer b.v.), 40.93 g of methyl *n*-amyl ketone and the calculated amount of catalyst were thoroughly mixed. To this container 39.42 g of an isocyanate (Desmodur® LS2025 from Bayer) was added.

10 From the mixture, drawdowns (wet film thickness 60 micrometre) on glass plates were made. Each plate was then cured and the hardness of the resulting film measured. The viscosity of the remaining mixture was then measured using a Brookfield viscometer every 0.5 hr.

**Viscosity of Hydroxyl Containing Polymer / Isocyanate Mixture vs. Time**

Time (hrs)	Comparative Catalyst (0.006g)	Catalyst A (0.073g)
0	138.3	135
0.5	156.7	146.7
1	233	156.7
1.5	226.7	156.7
2	256.7	156.7
2.5	306.7	156.7
3	390	156.7
3.5	425	156.7

**Film Hardness by Pendulum Testing of Resulting Films**

Cure Schedule	Comparative Catalyst	Catalyst A
ambient 264hrs	137 s	144 s
ambient 336hrs	146 s	160 s

**EXAMPLE 3**

The same catalyst and comparative catalyst as in Example 1 were used.

5      **Testing in Film Formation of the Catalyst (at an addition level to give molar % Zr equal to % Sn)**

109.4g of an acrylic resin (Joncryl 907 from S. C. Johnson Polymer b.v.), 46.1g butyl acetate and the calculated amount of catalyst were thoroughly mixed. To this container, 24.4g of an isocyanate (Tolonate® HDT from Rhone Poulenc) was added. From  
 10 the mixture, drawdowns (wet film thickness 60 micrometre) on glass plates were made. Each plate was then cured and the hardness of the resulting film measured. The viscosity of the remaining mixture was then measured using a Brookfield viscometer every 0.5hr.

**Viscosity of Hydroxyl Containing Polymer / Isocyanate Mixture vs. Time**

Time (hrs)	Comparative Catalyst (0.005g)	Catalyst A (0.061g)
0	163	165
0.5	178	165
1	197	165
1.5	212	165
2	237	165
2.5	300	173
3	383	173
3.5	405	173

**Film Hardness by Pendulum Testing of Resulting Films**

Cure Schedule	Comparative Catalyst	Catalyst A
Ambient 192h	171 s	180 s

**EXAMPLE 4**

**Preparation of Catalyst B**

5           1 mol of tetra-n-propyl zirconium (Tilcom® NPZ from Tioxide Specialties Ltd.) was added to a 1litre flask placed in cold water bath and 1 mol of acetylacetone was added over a period of one hour whilst the mixture was stirred. The resulting product was a pale yellow liquid.

0.01 mol of the product was added to a 50ml flask placed in a cold water bath and  
 10 0.1 mol of pentaerythritol *tetrakis*-(mercaptopropionate) was added. The resulting product was a clear mobile liquid. The zirconium content of the catalyst was measured at 1.63%.

**Preparation of Catalyst C**

1 mol of tetra-n-propyl zirconium (Tilcom® NPZ from Tioxide Specialties Ltd.) was added to a 1 litre flask placed in cold water bath and 1 mol of ethylacetoacetate was added over a period of one hour whilst the mixture was stirred. The resulting product was a pale yellow liquid.

0.01 mol of the product was added to a 50ml flask placed in a cold water bath and 0.2 mol of pentaerythritol *tetrakis*-(mercaptopropionate) was added. The resulting product was a clear mobile liquid. The zirconium content of the catalyst was estimated at 0.77%.

**Testing in Film Formation of the Catalyst (at an addition level to give equal molar % of Zr)**

104.4g of an acrylic resin (Joncryl 902 from S. C. Johnson Polymer b.v.), 48.1g butyl acetate and the calculated amount of catalyst were thoroughly mixed. To this container, 30.34g of an isocyanate (Tolonate® HDT from Rhone Poulenc) was added. From the mixture, drawdowns (wet film thickness 60 micrometre) on glass plates were made. Each plate was then cured and the hardness of the resulting film measured. The viscosity of the remaining mixture was then measured using a Brookfield viscometer every 0.5hr.

**Viscosity of Hydroxyl Containing Polymer / Isocyanate Mixture vs. Time**

Time (hrs)	Catalyst B (0.62g)	Catalyst C (1.31g)
0	185	177
0.5	185	177
1	185	177
1.5	211	192
2	231	192
2.5	280	213
3	315	213

Film Hardness by Pendulum Testing of Resulting Films

Cure Schedule	Catalyst B	Catalyst C
100°C / 0.5hr	191 s	180 s
Ambient 168hr	171 s	180 s

EXAMPLE 5Preparation of Catalyst D

A flask was charged with 449.6g of n-propyl zirconate (Tilcom® NPZ from Tioxide Specialties Limited; 20.3% Zr content) and placed in a cold water bath. 5 Ethylacetoacetate (130g) was added over a period of one hour whilst the mixture was stirred. The resulting product was a pale yellow liquid.

A separate flask was then charged with 289.8g of this mixture and 2-isopropyl-hydroxyethyl-1,3-oxazolidine (Incozol®3 from Industrial Copolymers Ltd.) 10 (159g) was added to the mixture whilst the mixture was stirred. The released solvent (n-propanol) was then removed by rotary evaporation under reduced pressure to leave a pale yellow oil. The zirconium content of the product was measured at 13.4%.

Preparation of Catalyst E

A flask was charged with 449.6g mole of n-propyl zirconate (Tilcom® NPZ 15 from Tioxide Specialties Limited; 20.3% Zr content) and placed in a cold water bath. Ethylacetoacetate (130g) was added over a period of one hour whilst the mixture was stirred. The resulting product was a pale yellow liquid.

A separate flask was then charged with 145.2g of this mixture and 2-isopropyl-N-hydroxyethyl-1,3-oxazolidine (Incozol® 3 from Industrial Copolymers Ltd.) 20 (159g) was then added to the mixture whilst the mixture was stirred. The released solvent (n-propanol) was then removed by rotary evaporation under reduced pressure to leave a pale yellow oil. The zirconium content of the product was measured at 9.34%.

Comparative Catalyst

Dibutyl tin dilaurate (source Aldrich Chemicals) was used as the 25 comparative catalyst.

Testing in film formation of the catalysts at an addition levels to give equivalent% Zr to % Sn (molar)

104.4g of a acrylic resin (Joncryl 902 from S.C. Johnson Polymer b.v.), 48.1g of butyl acetate and the calculated amount of catalyst were thoroughly mixed. To this



container 30.34g of an isocyanate (Tolonate® HDT from Rhone Poulenc) was added. From the mixture, drawdowns (wet film thickness 60 micrometre) on glass plates were made. Each plate was then cured and the hardness of the resulting film measured. The viscosity of the remaining mixture was then measured using a Brookfield viscometer at 5 time periods of 0.5 hrs.

**Viscosity of Hydroxyl Containing Polymer / Isocyanate Mixture vs. Time**

Time (hrs)	Comparative Catalyst (0.054g)	Catalyst D (0.06g)	Catalyst E (0.086g)
0	180	158.3	165
0.5	445	161.7	170
1	1000	180	196.7
1.5		196.7	213.3
2		211.7	248.3
2.5		238.3	280
3		293.3	343.3
3.5		311.7	368.3
4		331.7	406.6

**Film Hardness by Pendulum Testing of Resulting Films**

Cure schedule: 168 hrs, ambient.

Dibutyl tin dilaurate	199 s
Catalyst D	182 s
Catalyst E	197 s

**EXAMPLE 6**

10 **Preparation of Catalyst F**

A flask was charged with 449.6g of n-propyl zirconate (Tilcom® NPZ from Tioxide Specialties Limited; 20.3% Zr content) and placed in a cold water bath. Ethylacetoacetate (130g) was added over a period of one hour whilst the mixture was stirred. The resulting product was a pale yellow liquid.

15 A separate flask was then charged with 289.8g of this mixture and 2-isopropyl-N-hydroxyethyl-1,3-oxazolidine (Incozol® 3 from Industrial Copolymers Ltd.)

(159g) was added to the mixture whilst the mixture was stirred. The released solvent (n-propanol) was then removed by rotary evaporation under reduced pressure to leave a pale yellow oil. The zirconium content of the product was measured at 13.4%.

#### Comparative Catalyst

- 5 Dibutyl tin dilaurate (source Aldrich Chemicals) was used as the comparative catalyst.

#### Testing in Film Formation of the Catalysts at an addition level to give equivalent

##### % Zr to % Sn (molar)

- 96g of a acrylic resin (Joncryl 922 from S.C. Johnson Polymer b.v.), 0.53g of  
 10 BYK 320 (BYK-Chemie GmbH), 47.47g of butyl acetate and the calculated amount of catalyst were thoroughly mixed. To this container, 39.19g of an isocyanate (Tolcnate® HDT LV from Rhone Poulenc) was added. From the mixture, drawdowns (wet film thickness 60 micrometre) on glass plates were made. Each plate was then cured and the hardness of the resulting film measured. The viscosity of the remaining mixture was then  
 15 measured using a Brookfield viscometer at time periods of 0.5 hrs.

#### Viscosity of Hydroxyl Containing Polymer / Isocyanate Mixture vs. Time

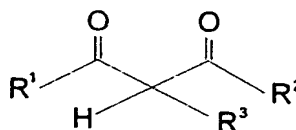
Time (hrs)	Comparative Catalyst (0.073g)	Catalyst F (0.079g)
0	73.3	83.3
0.5	160.0	113.3
1	1093	295

#### Film Hardness by Pendulum Testing of Resulting Films

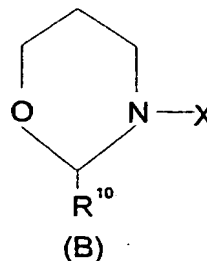
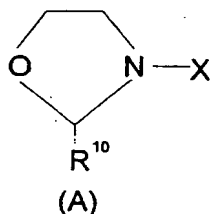
Cure Schedule	Comparative Catalyst	Catalyst F
100°C / 0.5 hr	166 s	175 s
100°C / 0.5 hr then 168 hrs ambient	199 s	206 s
168 hrs ambient	208 s	210 s

**CLAIMS**

1. A catalyst comprising the reaction product of:  
 (a) the reaction product of a titanium, zirconium, hafnium or aluminium orthoester and a  $\beta$ -diketone or  $\beta$ -ketoester having the general formula



- 5 where  $R^1$ ,  $R^2$  and  $R^3$  may be independently selected from the group consisting of hydrogen and alkyl, aryl, cycloalkyl, alkoxy, aryloxy, hydroxyalkyl, alkoxyalkyl and hydroxyalkoxyalkyl groups containing up to eight carbon atoms; and  
 (b) a complexing agent selected from a mercapto compound or an oxazolidine or  
 10 a tetrahydro-oxazine having the general formula (A) or (B) respectively



or mixtures thereof.

2. A catalyst according to claim 1 characterised in that the orthoester has the formula  $M(OR)_4$  in which M is titanium or zirconium and R is an alkyl group, a cycloalkyl  
 15 group or an aryl group.
3. A catalyst according to claim 1 or 2 characterised in that the  $\beta$ -diketone or  $\beta$ -ketoester is acetylacetone, methylacetoacetate, ethylacetoacetate or *tert*-butylacetoacetate.
4. A catalyst according to any one of the preceding claims characterised in that the  
 20 orthoester of titanium, zirconium, hafnium or aluminium and the  $\beta$ -diketone or  $\beta$ -ketoester are present in the reaction product in a molar ratio in the range 1 : 0.5 to 1 : 4, orthoester to  $\beta$ -diketone or  $\beta$ -ketoester.

5. A catalyst according to any one of the preceding claims characterised in that the mercapto compound is trimethylolpropane *tris*-(3-mercaptopropionate), pentaerythritol *tetrakis*-(3-mercaptopropionate), ethylene glycol *bis*-(3-mercaptopropionate) or pentaerythritol *tetrakis*-(2-mercaptoacetate).
- 5 6. A catalyst according to any one of the preceding claims characterised in that the complexing agent is an oxazolidine of formula (A) in which R<sup>10</sup> is hydrogen or an alkyl group containing up to 8 carbon atoms and X is a hydroxyalkyl group containing up to 6 carbon atoms.
7. A method of curing a composition comprising reacting a hydroxyl containing  
10 polymer or mixture of hydroxyl containing polymers with an isocyanate containing compound or a mixture of isocyanate containing compounds characterised in that the reaction is catalysed by a catalyst according to any one of the preceding claims.
8. A method according to claim 7 characterised in that the catalyst is present in an amount in the range 0.005 per cent to 0.5 per cent by weight with respect to weight of the  
15 composition.
9. A method according to claim 7 or 8 characterised in that the hydroxyl containing polymer is a polyester, a polyesteramide, a polyether, a siloxane as herein defined or a silicone as herein defined having hydroxyl functionality or a copolymer thereof.
10. A method according to any one of claims 7 to 9 characterised in that the  
20 isocyanate containing compound is an aromatic, aliphatic or mixed aliphatic/aromatic isocyanate.
11. A method according to any one of claims 7 to 10 characterised in that the composition contains isocyanate groups and hydroxyl groups in the range 1 : 2 to 2 : 1, isocyanate groups to hydroxyl groups.
- 25 12. A method according to any one of claims 7 to 11 characterised in that a solvent or a plasticiser is present in the composition.
13. A method according to any one of claims 7 to 12 characterised in that a plasticiser ester is present in the composition in an amount in the range 5 to 10% by weight.
14. A method according to any one of claims 7 to 13 characterised in that the  
30 composition contains an opacifying pigment or an extender.
15. A method according to any one of claims 7 to 14 characterised in that the composition is cured by heating at a temperature in the range 50°C to 150°C for a period of 1 to 30 minutes.

# INTERNATIONAL SEARCH REPORT

Inter. Application No  
PCT/GB 97/02565

A. CLASSIFICATION OF SUBJECT MATTER  
IPC 6 C08G18/22 C08K5/00 B01J31/38

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C08G C08K B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 391 937 A (FALENDER JAMES R ET AL) 5 July 1983	1
Y	see column 3, line 29 - column 5, line 32 see column 8, line 62 - column 9, line 3 see table 1	2-6
Y	---	
A	GB 869 988 A (ICI LTD.) 7 June 1961  see page 2, line 1 - page 2, line 43 see examples 8,11	1-6 7-15
Y	---	
A	GB 890 280 A (ICI LTD.) 28 February 1962 see page 2, line 34 - page 2, line 66 see examples 2-4	1-6 7-15
Y	---	
A	GB 951 949 A (AEROJET CORP.) 11 May 1964 see table IX	1-6 7-15
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

### \* Special categories of cited documents :

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
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- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*Z\* document member of the same patent family

Date of the actual completion of the international search

19 November 1997

Date of mailing of the international search report

10. 12. 97

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/GB 97/02565

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	see column 3, line 29 - column 3, line 75 see claims 1,5	2-6
	see column 1, line 25 - column 2, line 7 ---	1-15
A	EP 0 603 628 A (BAYER AG) 29 June 1994 see page 2, line 23 - page 2, line 48 see page 3, line 35 - page 4, line 40 see claims 1,5,8 ---	1-15
A	EP 0 316 893 A (HUELS CHEMISCHE WERKE AG) 24 May 1989 see examples 1,2 ---	1-6
Y	US 4 788 083 A (DAMMANN LAURENCE G ET AL) 29 November 1988	7-15
A	see figure 1 see column 3, line 51 - column 4, line 25 see claims 1,3,5 -----	

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PCT/GB 97/02565

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